IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Application of

Tsuneo YASHIKI, et al.

Serial No. 10/025,548

Filed: December 26, 2001

For: SOLID TITANIUM CATALYST COMPONENT, ETHYLENE POLYMERIZATION CATALYST CONTAINING THE SAME, AND ETHYLENE POLYMERIZATION PROCESS

Group Art Unit: 1711

Examiner: Caixia Lu

Honorable Commissioner of Patents and Trademarks
United States Patent and Trademark Office
Washington, D. C. 20231

Sir:

DECLARATION UNDER 37 CFR 1.132

I, Toshiyuki TSUTSUI, declare and state that:

1. I am a co-worker of the inventors of the invention described in the above-identified application.

2. In March 1979, I was graduated from Osaka University, Engineering Department of Applied Chemistry, and received a degree of Bachelor of Engineering from the Osaka University.

In April 1981, I was graduated from the graduate course of the Osaka University, Engineering Research Department, and

received a degree of Master of Engineering from the Osaka University.

Since April 1981, I have been an employee of MITSUI Petrochemical Industries Ltd., which has been named MITSUI Chemicals, Inc. and till the present time, I have been engaged in the research and development work concerning polymerization of olefins in Iwakuni Polymer Research Laboratory.

3. I carried out the following experiment in order to demonstrate the superiority of the ethylene polymerization catalyst according to the present application.

Experiments

Experiment 1

Preparation of Solid titanium catalyst

4.8 Grams (50 mmol) of anhydrous magnesium chloride, 25 ml of decane and 23.4 ml (150 mmol) of 2-ethylhexyl alcohol were reacted with each other under heating at 130 ℃ for 2 hours, to give a homogeneous solution. Thereafter, to the solution was added 1.1 g (7.5 mmol) of phthalic anhydride, the mixture was stirred for another 1 hour at 130 ℃, so that the phthalic anhydride was dissolved in the homogeneous solution.

The whole amount of the homogeneous solution obtained above was cooled to room temperature and then dropwise added to 200 ml (1.8 mol) of titanium tetrachloride maintained at -20 ℃, over a period of 1 hour. After the dropwise addition was completed, the temperature of the

resulting mixture was elevated to 110 ℃ over a period of 4 hours. When the temperature reached to 110 ℃, 2.7 ml (12.5 mmol) of diisobutylphthalate was added.

The mixture was stirred at a current temperature for another 2 hours. After the 2-hour reaction was completed, a solid produced was separated by hot filtration. The obtained solid was resuspended in 200 ml of titanium tetrachloride, the resulting suspension was stirred again with heating for 2 hours at 110 ℃.

After the reaction was completed, a solid produced was separated again by hot filtration. The solid was sufficiently washed with decane (110 ℃) and hexane (ambient temperature) until any titanium compound liberated in the washing liquid was not detected.

The composition of the solid titanium catalyst component thus obtained was 3.0 wt% of titanium, 57 wt% of chloride, 18 wt% of magnesium, and 21 wt% of diisobutylphthalate. no - organosilicon

Polymerization

The polymerization was conducted in the same manner as shown in Example 1 of the present application.

As a result, 8.5 g of a polymer having an MFR of 1.1 g/10 min was obtained. The catalytic activity of the catalyst was 1060 g-polymer/g-catalyst. what about based on Ti?

Experiment 2

Preparation of Solid titanium catalyst

A catalyst was prepared in accordance with Example 1 of the present application.

As a result, the composition of the catalyst thus obtained was 6.2 wt% of titanium, 16 wt% of magnesium, 61 wt% of chloride, 0.2 wt% of silicon, 1.1 wt% of ethoxy group, and 3.0 wt% of 2-ethylhexoxy group.

Polymerization

A stainless-steel autoclave having an internal volume of 2 liter, equipped with a stirrer was thoroughly purged with nitrogen. Therein was placed 1 liter of n-heptane. The autoclave was heated to 180 ℃, and ethylene was added until total pressure inside the autoclave became 12.5 kg/cm^2. Further, 0.4 mmol of triethylaluminum and 0.02 mmol in terms of titanium atom of the above obtained solid titanium catalyst was added to start a polymerization. The polymerization was conducted for 5 minutes at 180 ℃, while continuously feeding ethylene to keep the total pressure at 12.5 kg/cm^2.

After the completion of the polymerization, the resulting polymer was introduced into the excess methanol to precipitate the polymer. The reaction mixture was filtered to separate the polymer formed. The polymer was dried at 60 ℃ under reduced pressure and 44.0 g of the polymer was gained. The catalytic activity of the catalyst was 2810 g-polymer/g-catalyst, in particular, 45500 g-polymer/g-Ti

6.2% Ti invention

Experiment 3

Preparation of the catalyst component A9 of USP-5,278,118

A1 is cited in the rejection

To a 100 ml glass flask thoroughly purged with nitrogen were charged 4.8 g of anhydrous $MgCl_2$ and 38 g of $AlEtCl_2$, and

the mixture was heated to 120 ℃. The mixture was stirred for 3 hours so that $MgCl_2$ was completely dissolved.

To another 400 ml glass flask were charged 25.5 g of $Ti(O\text{-}n\text{-}Bu)_4$ and 50 ml of hexane, and the mixture was cooled to 0 ℃. To the latter mixture was added the solution of $MgCl_2$ over a period of 4 hours. The resulting mixture was then heated for 1 hour at 60 ℃. By this operation a solid component was precipitated. The supernatant was removed by decantation, and the resulting solid was repeatedly washed with 50 ml of hexane for four times.

17 Grams of the resulting solid component was suspended in 50 ml of toluene, and thereto was added 2.2 g of dimethoxydiphenylsilane. Then, the suspension was slowly heated to 80 ℃, was kept stirred at this temperature for 2 hours. Thereafter, the supernatant was removed by decantation, and the resulting solid was repeatedly washed with 50 ml of hexane for four times.

The resulting solid was dried at 40 ℃ under reduced pressure for 3 hours, to obtain a catalyst component having 17.6 wt% of titanium, 5.5 wt% of magnesium, 2.1 wt% of aluminum, 54 wt% of chloride, and 7 wt% of butoxy group.

Polymerization

Polyethylene was polymerized in the same manner as Example 1 of the present application.

As a result, 6.2 g of a polymer having an MFR of 0.86 g/10 min was obtained. The catalytic activity of the catalyst was 4520 g-polymer/g-catalyst.

A9 (17.6% Ti)

in A9, 2.3×10³ g/g cat
Cat activity //

The undersigned declares further that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This day of September, 2002

Toshiyuki Tsutsui